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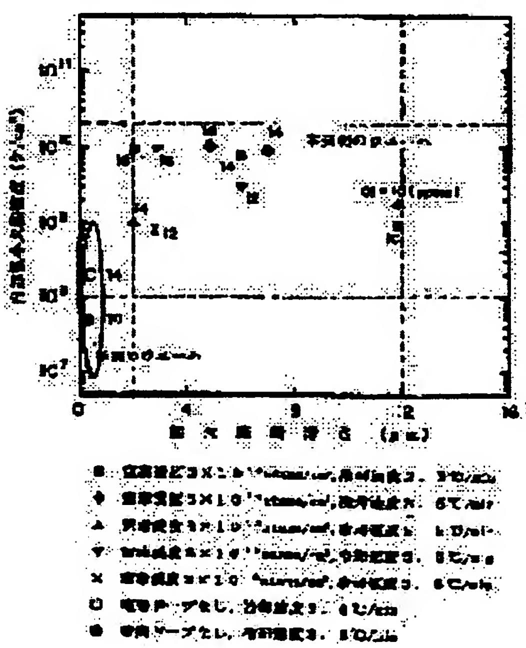
(54) SILICON SINGLE CRYSTAL WAFER AND ITS PRODUCTION



(57)Abstract:

PROBLEM TO BE SOLVED: To enlarge the control region of defect-free layer depth and fine defect density of the inside in a CZ silicon wafer.

SOLUTION: This silicon wafer is a silicon wafer which is obtained from a silicon single crystal rod grown by doping with nitrogen by CZ method, has 2-12 μm defect-free layer depth after gettering heat treatment and after device production and heat treatment of silicon wafer and 1×108 to 2×1010 defects/cm3 internal fine defect density after gettering heat treatment and after device production and heat treatment. This method for producing a silicon wafer comprises growing a silicon single crystal rod doped with nitrogen by CZ method while controlling a nitrogen concentration, an

oxygen concentration and a cooling rate and processing the silicon single crystal rod into a wafer.

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CLAIMS

[Claim(s)]

[Claim 1] The silicon-single-crystal wafer characterized by being the silicon-single-crystal wafer which sliced and obtained the silicon-single-crystal rod

which doped nitrogen with the Czochrlski method and was raised, and for the defect-free layer depth after gettering heat treatment of this silicon-single-crystal wafer or device manufacture heat treatment being 2-12 micrometers, and 1x108 to 2x1010 internal minute defect density /after gettering heat treatment or device manufacture heat treatment being [cm] 3.

[Claim 2] The silicon-single-crystal wafer indicated to the claim 1 characterized by the nitrogen concentration of the aforementioned silicon-single-crystal wafer being 1x1012 - 1x1015 atoms/cm3.

[Claim 3] The silicon-single-crystal wafer indicated to the claim 1 characterized by the nitrogen concentration of the aforementioned silicon-single-crystal wafer being 1x1013 - 1x1014 atoms/cm3.

[Claim 4] The silicon-single-crystal wafer indicated in any 1 term of the claim 1 characterized by the oxygen density of the aforementioned silicon-single-crystal wafer being 9 - 17ppma, or a claim 3.

[Claim 5] The silicon-single-crystal wafer indicated in any 1 term of the claim 1 characterized by the aforementioned silicon-single-crystal rod being a single crystal rod which was controlled by the range of 1.0-4.5 degrees C/min, and was raised in the cooling rate from 1150 degrees C to 1080 degrees C at the time of a crystal growth, or a claim 4.

[Claim 6] The manufacture method of the silicon-single-crystal wafer characterized by raising the silicon-single-crystal rod which doped nitrogen with the Czochrlski method in the manufacture method of a silicon-single-crystal wafer, controlling nitrogen concentration, an oxygen density, and a cooling rate, slicing this silicon-single-crystal rod, and processing it into a wafer.

[Claim 7] The manufacture method of the silicon-single-crystal wafer indicated to the claim 6 characterized by controlling the nitrogen concentration doped on this single crystal rod to 1x1012 - 1x1015 atoms/cm3 in case the silicon-single-crystal rod which doped nitrogen with the aforementioned Czochrlski method is raised.

[Claim 8] The manufacture method of the silicon-single-crystal wafer indicated to the claim 6 characterized by controlling the nitrogen concentration doped on this single crystal rod to 1x1013 - 1x1014 atoms/cm3 in case the silicon-single-crystal rod which doped nitrogen with the aforementioned Czochrlski method is raised.

[Claim 9] The manufacture method of the silicon-single-crystal wafer indicated in any 1 term of the claim 6 characterized by controlling the oxygen density contained on this single crystal rod to 9 - 17ppma in case the silicon-single-crystal rod which doped nitrogen with the aforementioned Czochrlski method is raised, or a claim 8.

[Claim 10] The manufacture method of the silicon-single-crystal wafer indicated in any 1 term of the claim 6 characterized by controlling the cooling rate from 1150 degrees C to 1080 degrees C at the time of the crystal growth of this single crystal rod in the range of 1.0-4.5 degrees C/min in case the silicon-single-crystal rod which doped nitrogen with the aforementioned Czochrlski method is raised, or a claim 9.

[Translation done.]
* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] In case this invention pulls up a silicon single crystal with the Czochrlski method (CZ process), it relates to the technology of manufacturing the silicon-single-crystal wafer which has desired quality, by doping nitrogen, and controlling nitrogen concentration, an oxygen density, and a cooling rate, and performing a crystal growth.
[0002]
[Description of the Prior Art] As a wafer for producing devices, such as a semiconductor integrated circuit, the silicon-single-crystal wafer mainly raised by the Czochrlski method (CZ process) is used. If a crystal defect exists in such a silicon-single-crystal wafer, a poor pattern will be caused at the time of semiconductor-device production. Since especially the pattern width of face in the device integrated by altitude in recent years is a very detailed thing of 0.3 micrometers or less, at the time of such pattern formation, also in existence of the crystal defect of 0.1-micrometer size, it will cause a poor pattern and will reduce the production yield or quality characteristic of a device remarkably. Therefore, the crystal defect which exists in a silicon-single-crystal wafer must make size small as much as possible.

[0003] Into the silicon single crystal raised by the CZ process, it is recently reported especially that the crystal defect which is called Grown-in defect and which was introduced into the crystal growth exists. It is thought that the main causes of generating of such a crystal defect are precipitation-of-oxygen objects which are the flocs of the oxygen atom mixed from the cluster or quartz crucible of an atomic hole condensed during single crystal manufacture. If these crystal defects exist in the surface section of the wafer with which a device is formed, since they will turn into an injurious defect which degrades a device property, it is desirable to produce the wafer which has the defect-free layer (DZ) which reduces such a crystal defect and has sufficient depth in the surface section.

[0004] Moreover, if heavy-metal impurities, such as Fe and Cu, exist in the surface section of a silicon-single-crystal wafer, degradation of a device property will be produced at the time of device production. Therefore, as a gettering site, an internal minute defect is deposited in the bulk section of a silicon wafer, and the in thorin chic gettering (IG) which removes a heavy-metal impurity becomes important at it. In order to make this in thorin chic gettering effective, it is needed to make the internal minute defect (BMD) of sufficient density for the bulk section of a wafer form. In addition, an internal minute defect here points out minute defects which induction is carried out to the precipitation-of-oxygen object and precipitation of oxygen which exist during bulk, and are generated, such as transposition and a stacking fault.

[0005] In manufacture of a silicon semiconductor wafer, the depth of the defect-free layer on the front face of a wafer where a device is produced after gettering heat treatment or device process heat treatment, and the density of the internal minute defect inside the wafer used as a gettering site serve as an important element from the above point.

[0006] It was known that this defect-free layer depth and internal minute defect density will be dependent on the oxygen density of the silicon single crystal raised by the CZ process or the cooling rate in a silicon single crystal growth (growth rate). Therefore, mainly controlling an oxygen density and a cooling rate was carried out to conventionally controlling the defect-free layer depth and internal minute defect density of a silicon wafer.

[0007]

[Problem(s) to be Solved by the Invention] However, since the silicon-single-crystal wafer obtained from the silicon-single-crystal rod raised by the method of controlling such an oxygen density and a cooling rate had the large size of crystal defects, such as a Grown-in defect, a crystal defect was not fully able to be extinguished with subsequent

gettering heat treatment etc. As the result, the defect-free layer depth of the conventional silicon-single-crystal wafer had become an about 0.5-micrometer shallow thing at the maximum.

[0008] Moreover, in the conventional method, in the case of the wafer of the hyperoxia concentration about 20ppma (JEIDA:Japan Electronic Industry Development Association specification), although the internal minute defect density after heat treatment became about [1x1010 //cm] three at the maximum, since the crystal defect of an oxygen reason near the front face remained, it had become the cause of reducing the yield of a device. Moreover, with the wafer of 9 - 17ppma, in order for the internal minute defect density after heat treatment to stop about [1x109 //cm] at three at the maximum and to obtain sufficient gettering effect, internal minute defect density is insufficient of the oxygen densities usually used for a device. Therefore, the fall of the device process yield resulting from the heavy metal contamination on the front face of a wafer was a problem.

[0009] In view of such a trouble, it succeeded in this invention, it expands sharply the controllable range of the defect-free layer depth and internal minute defect density in the silicon-single-crystal wafer produced by the CZ process, and aims at obtaining a quality silicon-single-crystal wafer.

[0010]

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, invention indicated to the claim 1 of this invention It is the silicon-single-crystal wafer which sliced and obtained the silicon-single-crystal rod which doped nitrogen with the Czochrlski method and was raised. The defect-free layer depth after gettering heat treatment of this silicon-single-crystal wafer or device manufacture heat treatment is 2-12 micrometers. And it is the silicon-single-crystal wafer characterized by 1x108 to 2x1010 internal minute defect density /after gettering heat treatment or device manufacture heat treatment being [cm] 3.

[0011] Thus, the silicon-single-crystal wafer which consists of the silicon-single-crystal rod which doped nitrogen with the Czochrlski method and was raised The defect-free layer depth after gettering heat treatment or device manufacture heat treatment by 2-12 micrometers And since the internal minute defect density after gettering heat treatment or device manufacture heat treatment is sharply set controllable to 3 in the latus range compared with the silicon-single-crystal wafer of the former 1x108 to 2x1010 pieces /cm, The field in which device formation is possible is large, and serves as a silicon-single-crystal wafer which has high gettering capacity.

[0012] In addition, heat treatment performed even before going into a device process,

after processing the raised silicon-single-crystal rod into a wafer is named generically, and it mainly aims at disappearance of the crystal defect near [by the out diffusion of impurity oxygen] the front face for gettering heat treatment here. Device heat treatment names generically heat treatment performed by the device manufacturing process, after processing gettering heat treatment and others to a wafer.

[0013] In this case, as indicated to the claim 2 of this invention, it is desirable that the nitrogen concentration of the aforementioned silicon-single-crystal wafer is 1x1012 - 1x1015 atoms/cm3. In order to make size of a crystal defect small and to suppress growth of a defect In order it is desirable to make nitrogen concentration into three or more 1x1010 atoms/cm and to make it not become the hindrance of single-crystal-izing of a silicon single crystal Although it is desirable to consider as three or less 5x1015 atoms/cm, the nitrogen concentration of the range of this 1x1012 - 1x1015 atoms/cm3 Since it is the nitrogen concentration most effective for suppression of growth of a crystal defect, if the nitrogen concentration of a wafer is this range, size of a crystal defect can be made small enough and the defect-free layer depth after gettering heat treatment can be made deep.

[0014] In this case, it is still more desirable if the nitrogen concentration of the aforementioned silicon-single-crystal wafer is 1x1013 - 1x1014 atoms/cm3 as indicated to the claim 3 of this invention. Since an OSF nucleus can be more certainly extinguished after nitrogen concentration is given to three or less 1x1014 atoms/cm then gettering heat treatment, or device manufacture heat treatment, the property of the device formed on such a wafer becomes what has still higher reliability. Moreover, when growing epitaxially on such a wafer front face, it also has the advantage which can suppress remarkably crystal defects, such as a stacking fault (SF) formed into the formed epitaxial layer, with this OSF disappearance. On the other hand, if nitrogen concentration is three or more 1x1013 atoms/cm, since three or more [1x109 //cm] are obtained certainly, the internal-defect density after gettering heat treatment or device manufacture heat treatment can expect much more gettering effect.

[0015] In this case, as indicated to the claim 4 of this invention, it is desirable that the oxygen density of the aforementioned silicon-single-crystal wafer is 9 - 17ppma. If the oxygen density of a silicon-single-crystal wafer is the value of this range, growth formation of a crystal defect can be suppressed further and formation of the precipitation-of-oxygen object in a defect-free layer can also be prevented. On the other hand, in the bulk section, since precipitation of oxygen is promoted by existence of nitrogen, even if it is the hypoxia concentration of about 9 ppmas which is the lower limit of the above-mentioned range, the IG effect can fully be demonstrated.

[0016] In this case, as indicated to the claim 5 of this invention, it is desirable that the aforementioned silicon-single-crystal rod is a single crystal rod which was controlled by the range of 1.0-4.5 degrees C/min, and was raised in the cooling rate from 1150 degrees C to 1080 degrees C at the time of a crystal growth. If the cooling rate from 1150 degrees C to 1080 degrees C after a crystal growth is the range of 1.0-4.5 degrees C/min, a crystal defect can be made small enough and the silicon wafer the defect-free layer depth after gettering heat treatment is 2-12 micrometers, and the range of whose 1x108 to 2x1010 internal minute defect density /is [cm] 3 can be manufactured. Moreover, if it is the cooling rate of this range, it is not necessary to make silicon single crystal-growth speed so late that it have influence on productivity.

[0017] Moreover, invention indicated to the claim 6 of this invention is the manufacture method of the silicon-single-crystal wafer characterized by raising the silicon-single-crystal rod which doped nitrogen with the Czochrlski method, controlling nitrogen concentration, an oxygen density, and a cooling rate, slicing this silicon-single-crystal rod, and processing it into a wafer in the manufacture method of a silicon-single-crystal wafer.

[0018] Thus, by controlling an oxygen density and not only a cooling rate but the amount of nitrogen dopes, and raising a silicon-single-crystal rod, the control range of the defect-free layer depth and internal minute defect density can be expanded sharply, and can manufacture the quality silicon-single-crystal wafer whose 1x108 to 2x1010 internal minute defect density /the defect-free layer depth is 2-12 micrometers, and is [cm] 3.

[0019] In this case, as indicated to the claim 7 of this invention, in case the silicon-single-crystal rod which doped nitrogen with the aforementioned Czochrlski method is raised, it is desirable to control the nitrogen concentration doped on this single crystal rod to 1x1012 - 1x1015 atoms/cm3, and if nitrogen concentration is controlled to 1x1013 - 1x1014 atoms/cm3 as indicated to the claim 8, it is much more desirable. Moreover, as indicated to the claim 9, as further indicated to the claim 10, it is desirable [it is desirable to control the oxygen density contained on this single crystal rod to 9 - 17ppma and] to control the cooling rate from 1150 degrees C to 1080 degrees C at the time of the crystal growth of this single crystal rod in the range of 1.0-4.5 degrees C/min.

[0020] Thus, in case the silicon-single-crystal rod which doped nitrogen is raised, the silicon-single-crystal wafer by which the defect-free layer depth is 2-12 micrometers certainly, and 1x108 to 2x1010 internal minute defect density /was controlled by 3 cm can be manufactured by controlling nitrogen concentration, an oxygen density, and a

cooling rate in the above-mentioned range.

[0021] Hereafter, this invention is further explained to a detail. In addition to controlling the oxygen density and cooling rate which were performed by the conventional method, this invention results research in completion in piles wholeheartedly by controlling the nitrogen concentration in a silicon single crystal based on the knowledge that the range which can control the defect-free layer depth and internal minute defect density is sharply expandable.

[0022] Conventionally, the defect-free layer depth and internal minute defect density of a silicon wafer were uncontrollable only in the very narrow range. Drawing 1 is drawing having shown the defect-free layer depth and internal minute defect density of a silicon-single-crystal wafer in the value of each parameters, such as an oxygen density, here.

[0023] It turns out that an oxygen density can control the defect-free layer depth and 0-0.5 micrometers of internal minute defect density by the wafer of 9 - 17ppma cm only in the narrow range 8x106 to 1x109 pieces /3 though an oxygen density is changed like the conventional method and a cooling rate is changed as shown in drawing 1 , respectively.

[0024] This cause suited the size of the crystal defect in a conventional method, the size of a precipitation-of-oxygen object, and its density. Drawing 2 (a) and (b) are drawings having shown typically the crystal defect in a silicon-single-crystal wafer, and the appearance of a precipitation-of-oxygen object, and drawing 2 (b) is drawing having shown the situation in the wafer by the conventional process. Although according to the conventional method the density of a crystal defect is low and there are few defects as shown in drawing 2 (b), a crystal defect with large size will occur. In subsequent gettering heat treatment, the crystal defect with this large size could not fully be removed, but had become the cause of making the defect-free layer depth thin. Moreover, the density of the precipitation-of-oxygen object in the wafer bulk section was low, and since the size was also small, gettering capacity became low.

[0025] Then, when the artificers of this invention raised a silicon single crystal with the Czochrlski method, they doped nitrogen, and they hit on an idea of controlling the amount. The defect-free layer depth and internal minute defect density in each parameter value of a silicon-single-crystal wafer of this invention were written together to drawing 1 . The defect-free layer depth of the wafer of this invention is 2-12 micrometers, in internal minute defect density, 1x108 to 2x1010 pieces/cm, it is wide range and drawing 1 shows [3] that is controllable.

[0026] Moreover, the situation in the wafer of this invention was shown in drawing 2 (a).

According to the method of this invention, as shown in drawing 2 (a), the density of a crystal defect is high, and although there are many defects, a crystal defect with small size generates it. The crystal defect with such small size is easily eliminable with subsequent gettering heat treatment etc. Therefore, let the defect-free layer depth be a sharply deep thing compared with the conventional wafer. In addition, in the bulk section of a wafer, since the precipitation-of-oxygen object with large size which is hard to dissolve with gettering heat treatment deposits in large quantities, the far high gettering effect can be acquired compared with the conventional wafer.

[0027] The silicon-single-crystal wafer of this invention has such a property because the nitrogen controlled by optimum dose is doped. That is, if nitrogen is doped in a silicon single crystal, condensation of the atomic hole in silicon is suppressed and it is pointed out that the size of a crystal defect contracts (T. 3 Abe and H.Takeno, Mat.Res.Soc.Symp.Proc.Vol.262, 1992). It is thought that this effect is for the condensation process of an atomic hole to shift to uneven nucleation from uniform nucleation. Therefore, if nitrogen is doped in case a silicon single crystal is raised by the CZ process, the silicon-single-crystal wafer into which the silicon single crystal and this which made size of a crystal defect very small were processed can be obtained.

[0028] On the other hand, it is also known that a nitrogen atom has the effect of making precipitation of oxygen promoting, in a crystal growth. (224 For example, F.Shimura and R.S.Hockett, Appl.Phys.Lett.48, 1986) . Therefore, by doping nitrogen in optimum dose, the precipitation-of-oxygen object density of the wafer bulk section can be raised, and the gettering capacity of a silicon-single-crystal wafer can be raised remarkably.

[0029] If nitrogen is doped in a silicon single crystal, it will be thought that the reason the crystal defect introduced into silicon decreases is as above-mentioned for the condensation process of an atomic hole to shift to uneven nucleation from uniform nucleation. Therefore, since the single-crystal-izing of a silicon single crystal itself may be checked when it is desirable to make it three or more 1x1010 atoms/cm which fully cause uneven nucleation and it exceeds 5x1015 atoms/cm3 which is a solid-solution limit community in a silicon single crystal, as for the concentration of the nitrogen to dope, it is desirable to make it not exceed this concentration.

[0030] Furthermore, as a result of the artificer of this invention repeating research and examination further about this nitrogen concentration, generating of a crystal defect was suppressed and the defect-free layer depth and nitrogen concentration effective for control of internal minute defect density found out that it was the range of 1x1012 - 1x1015 atoms/cm3. It is because the defect-free layer depth and internal minute defect density are easily controllable in the range of the wafer of this invention if it is such a

density range with the comparatively high concentration of the nitrogen to dope.

[0031] Furthermore, in addition, when the artificer of this invention continued research further about this nitrogen concentration, it made him clear that it is most effective to make the above-mentioned nitrogen concentration into 1x1013 - 1x1014 atoms/cm3. The artificers of this invention conducted the following experiments in order to discover the optimum value of nitrogen concentration.

(Experiment 1) The diameter of 8 inches, P type (boron dope), and the single crystal rod of a direction <100> were first pulled up by two kinds of pull-up speed 1.0 mm/min and 1.8 mm/min**s. The amount of the wafer with a silicon nitride film thrown in in a raw material so that nitrogen concentration may serve as 3x1012 - 1x1015 atoms/cm3 was adjusted at that time. And the silicon-single-crystal rod which was able to be pulled up was processed, and the silicon-single-crystal mirror-plane wafer was produced. All, the resistivity of the produced silicon-single-crystal mirror-plane wafer was about 10 ohm-cm, and the oxygen density was the range of 9 - 17ppma (JEIDA).

[0032] Next, 1100 degrees C and OSF heat-of-combustion processing for 60 minutes were performed to these wafers, the width of face of the OSF field generated on the front face was measured, and the measurement result was shown in drawing 3 . In addition, in drawing 3 , notation 1.0E+13 of a horizontal axis mean 1x1013. Drawing 3 shows that the field width of face which OSF generates [nitrogen concentration] in three or less 1x1014 atoms/cm is contracting extremely.

[0033] Moreover, about another wafer produced on the same conditions as the wafer which investigated OSF, without performing OSF oxidization, 800 degrees C, heat treatment (nitrogen-gas-atmosphere mind) of 4 hours, and 1000 degrees C and heat-of-combustion processing of 16 hours were performed, and the internal minute defect density of a wafer was evaluated by the below-mentioned OPP method. Consequently, it turns out that the internal minute defect density of three or more [1x109 //cm] is certainly obtained for nitrogen concentration by three or more 1x1013 atoms/cm.

[0034] (Experiment 2) Except that nitrogen concentration was 1x1013 - 1x1015 atoms/cm3, the silicon-single-crystal mirror-plane wafer of the same specification as experiment 1 was produced, and the temperature up was carried out by 6 degrees C/min in 100% atmosphere of hydrogen gas as gettering heat treatment, and it classified into what performed heat treatment cooled by 3 degrees C/min, and the thing which does not perform the heat treatment, after maintaining at 1200 degrees C for 60 minutes. Next, the epitaxial growth system was used for the front face of each wafer, and silicon epitaxial growth with a thickness of 15 micrometers was performed at 1090 degrees C.

And SP1 (tradename by the KLA ten call company) performed stacking-fault (SF) density of the front face after epitaxial growth, and the result was shown in drawing 4 . In addition, also in drawing 4 , notation 1.0E+13 of a horizontal axis mean 1x1013, for example.

[0035] Drawing 4 shows that it is not concerned with the existence of raising speed and gettering heat treatment, but the stacking-fault (SF) density on the front face of an epitaxial layer can be sharply reduced if nitrogen concentration is three or less 1x1014 atoms/cm.

[0036] The above thing is known when the above experimental result is summarized. Since most nuclei of OSF (oxidization induction stacking fault) which existed in the wafer front face from the first by performing gettering heat treatment or device manufacture heat treatment disappear, OSF occurring and having big influence on a device property has few wafers with which nitrogen was doped.

[0037] However, the field where OSF generates nitrogen concentration since there are very few OSF nuclei even if it is in the state before three or less 1x1014 atoms/cm then gettering heat treatment, or device manufacture heat treatment can be extinguished nearly completely over the whole wafer surface. Therefore, since an OSF nucleus can be more certainly extinguished after gettering heat treatment or device manufacture heat treatment is performed, the property of the device formed on such a wafer becomes what has still higher reliability. In addition, the nucleus of OSF is a defect which is not detected as poor in the below-mentioned oxide-film proof-pressure characterization (TZDB, TDDB).

[0038] Moreover, it has crystal defects, such as a stacking fault (SF) formed into the epitaxial layer formed when nitrogen concentration was made into three or less 1x1014 atoms/cm and it grew epitaxially on the wafer front face with disappearance of an OSF nucleus, and the advantage which can be suppressed remarkably.

[0039] On the other hand, if nitrogen concentration is three or more 1x1013 atoms/cm, since three or more [1x109 //cm] are obtained certainly, much more gettering effect can certainly expect the internal-defect density after gettering heat treatment or device manufacture heat treatment.

[0040] Moreover, the artificer discovered that it was desirable to make an oxygen density into the range of 9 - 17ppma, in order to control the defect-free layer depth and internal minute defect density in the range of the wafer of this invention. It is because there is no danger that a precipitation-of-oxygen object detrimental to the defect-free layer in which a device is formed will be formed, after wafer processing and there is no fear of precipitation-of-oxygen objects running short and causing the fall of the gettering

effect and the fall of crystal intensity by making it 9 or more ppmas conversely, when this is made into the oxygen density of 17 or less ppmas. Therefore, as for the oxygen density of a silicon-single-crystal wafer, it is desirable that it is the range of 9 - 17ppma.

[0041] Furthermore, the artificer discovered that it was desirable to control the cooling rate from 1150 degrees C to 1080 degrees C at the time of a crystal growth to 1.0-4.5 degrees C/min, in order to control the defect-free layer depth and internal minute defect density in the range of the wafer of this invention. This is because the size of a crystal defect is greatly influenced by the pass time of the condensation temperature zone region of an atomic hole. If a cooling rate is made quicker than [1.0 degrees C /] min, the size of a crystal defect is reducible, and if cooling rates are below 4.5 degrees C / min, a dislocation free crystal can be grown up. Therefore, in order to control in the range of the wafer of this invention, it is desirable to control a cooling rate in the range of 1.0-4.5 degrees C/min. In addition, what is necessary is just to be able to find out the manufacture conditions which can produce a dislocation free crystal, even if it is a cooling rate 4.5 degrees C / more than min.

[0042]

[Embodiments of the Invention] What is necessary is to just be based on a well-known method which is indicated by JP,60-251190,A in this invention, in order to raise the silicon-single-crystal rod which doped nitrogen by the CZ process.

[0043] That is, although a CZ process is a method of pulling up slowly and raising the silicon-single-crystal rod of a request diameter, contacting seed crystal to the melt of the polycrystal silicon raw material held into the quartz crucible, and rotating this, it can dope nitrogen during a raising crystal by putting in the nitride in the quartz crucible beforehand, supplying a nitride in a silicon melt, or making a controlled atmosphere into the atmosphere containing nitrogen etc. Under the present circumstances, the amount of dopes under crystal is controllable by adjusting concentration or an installation time of the amount of a nitride, or nitrogen gas etc. In this way, it can also perform easily controlling to the nitrogen concentration of above-mentioned 1x1012 - above-mentioned 1x1015 atoms/cm3, or 1x1013 - 1x1014 atoms/cm3.

[0044] Moreover, as mentioned above, in case the silicon-single-crystal rod which doped nitrogen by the CZ process is raised in this invention, it is desirable to control the oxygen density contained on a single crystal rod in the range of 9 - 17ppma. In case a silicon-single-crystal rod is raised, the method of reducing the oxygen density to contain in the above-mentioned range should just be based on the method commonly used from the former. For example, it can consider as the above-mentioned oxygen density range easily by meanses, such as temperature distribution of reduction of a crucible rotational

frequency, the increase in an introductory quantity of gas flow, the fall of the ambient-pressure force, and a silicon melt, and adjustment of the convection current.

[0045] Moreover, as mentioned above, in case the silicon-single-crystal rod which doped nitrogen by the CZ process is raised in this invention, it is desirable to control the cooling rate in a crystal growth to 1.0-4.5 degrees C/min. In order to realize such [actually] crystal manufacture conditions, it is possible to carry out by the method of adjusting the pull-up speed of a crystal and making crystal-growth speed fluctuating. Or what is necessary is just to form the equipment which can cool a crystal with arbitrary cooling rates in the chamber of a CZ process silicon-single-crystal manufacturing installation. Methods, such as preparing a water-cooled ring in the equipment which sprays coolant gas and can cool a crystal as such a cooling system, or the fixed position on a melt side so that a crystal may be enclosed, are applicable. In this case, it can consider as above-mentioned cooling rate within the limits by adjusting the raising speed of the above-mentioned cooling method and a crystal.

[0046] In this way, in a CZ process, the nitrogen of request concentration is doped, the oxygen of request concentration is contained, and the silicon-single-crystal rod with which the crystal growth was made with the desired cooling rate can be obtained. After slicing this with cutting equipments, such as an inner circumference edge slicer or a wire saw, according to the usual method, it is processed into a silicon-single-crystal wafer through processes, such as beveling, wrapping, etching, and polish. of course -- ** these processes remain for having carried out instantiation listing, in addition may have various processes, such as washing, -- change of the order of a process -- according to the purposes, such as an ellipsis, change use of the process is carried out suitably in part

[0047] And by heat-treating the silicon-single-crystal wafer obtained in this way in subsequent gettering heat treatment and/or subsequent device manufacture heat treatment, the defect-free layer depth is 2-12 micrometers, and internal minute defect density can obtain the silicon-single-crystal wafer of this invention 1x108 to 2x1010 pieces /3, cm. Since the silicon-single-crystal wafer of this this invention has the deep defect-free layer which is a device production field, the flexibility of device production is high, and since it has high gettering capacity, the device yield also serves as a high wafer.

[0048]

[Example] Although the example and the example of comparison of this invention are given and being explained concretely hereafter, this invention is not limited to these.

(An example, example of comparison) By the CZ process, to the quartz crucible with a

diameter of 18 inches, raw material polycrystal silicon was charged, the conditions of the amount of nitrogen dopes, an oxygen density, and a cooling rate were changed, and the diameter of 8 inches, P type, a direction <100>, and 12 crystal rods of resistivity 10 ohm-cm were pulled up.

[0049] Control of the amount of nitrogen dopes was performed by throwing in the silicon wafer which has the silicon nitride film of the specified quantity beforehand in the raw material. Control of an oxygen density was performed by controlling crucible rotation during raising. Control of a cooling rate was performed by changing the pull-up speed of a single crystal rod, and changing crystal-growth speed.

[0050] From the single crystal rod obtained here, the wafer was cut down using the wire saw, beveling, wrapping, etching, and mirror-polishing processing were given, and conditions other than the amount of dopes of nitrogen, an oxygen density, and a cooling rate produced respectively two or more silicon-single-crystal mirror-plane wafers of 12 kinds of 8 inches diameters made almost the same.

[0051] In this way, gettering heat treatment was performed to the obtained silicon-single-crystal wafer. Gettering heat treatment in this case was performed by cooling at the rate of a temperature fall of 3 degrees C/min, after carrying out the temperature up of the silicon-single-crystal wafer to 50% of hydrogen to 1200 degrees C at the rate of a temperature up of 6 degrees C/min under the atmosphere which consists of argon 50% and maintaining it at 1200 degrees C for 60 minutes.

[0052] Then, the defect-free layer depth of these 12 kinds of silicon-single-crystal wafers was evaluated. Evaluation of this defect-free layer depth performed surface polish first, and the wafer into which the amount of polish removal from a front face was changed was prepared. With and SC-1 mixed liquor (1:1:20 mixed liquor of aqueous ammonia (NH4OH), hydrogen peroxide solution (H2O2), and ultrapure water) Minute COP is actualized by washing a wafer at the temperature of about 80 degrees C for 1 hour. The size which exists a wafer front face in the wafer front face in SP1 particle measuring device made from KLA/Tencor measured by counting the number of COPs about COP (Crystal Originated Particle) 0.10 micrometers or more. Polish removal was performed by 12-micrometer Fukashi for every micrometer.

[0053] Moreover, it carried out also by evaluating oxide-film proof-pressure quality like [depth / defect-free layer] the above about the wafer into which the amount of polish removal from a front face was changed. Evaluation of oxide-film proof-pressure quality made the rate of an excellent article at the time of measuring 100 electrodes in a wafer side the rate of a C-mode excellent article by using as an excellent article the C mode yield of TZDB (Time Zero Dielectric Breakdown), and the thing of 8 or more MV/cm of

dielectric-breakdown electric fields which produced the phosphorus dope polysilicon contest electrode (25nm of oxidization thickness, electrode area 8mm2) in detail, and were evaluated by judgment current-value 1 mA/cm2.

[0054] Moreover, gamma mode yield of TDDB (Time Dependent Dielectric Breakdown) also estimated. This produced the phosphorus dope polysilicon contest electrode (25nm of oxidization thickness, electrode area 4mm2), passed 2 continuously 0.01mA [/cm] stress current, and made the rate of an excellent article at the time of measuring 100 electrodes in a wafer side the rate of a gamma-mode excellent article by using as an excellent article what dielectric breakdown generates in two or more amount of charges 25 C/cm. And in evaluation of both TZDB and TDDB, the case where the rate of an excellent article was 90% or more was judged to be a defect-free layer.

[0055] Then, heat treatment which imitated device heat treatment to these 12 kinds of silicon-single-crystal wafers was performed. This heat treatment was nitrogen-gas-atmosphere mind about the silicon-single-crystal wafer, and after performing 800-degree C heat treatment for 4 hours, it was performed by performing 1000-degree C heat-of-combustion processing for 16 hours.

[0056] And the internal minute defect density of these 12 kinds of silicon-single-crystal wafers was evaluated. Measurement of this internal minute defect density was performed by the OPP (Optical Precipitate Profiler) method. This OPP method divides the laser beam which is a thing adapting the normal skiing type differential interference microscope, and came out of the light source first into the beam of the linearly polarized light from which two 90-degree phases which intersect perpendicularly differ with a polarizing prism, and it is made it to carry out incidence from a wafer mirror-plane side. If one beam crosses a defect at this time, a phase shift will arise and phase contrast with another beam will arise. A defect is detected by detecting this phase contrast with a polarization analyzer after wafer side transparency.

[0057] In this way, the obtained measurement result was shown in Table 1. About evaluation of the defect-free layer depth, the evaluation by the number of COPs estimated that even the depth with few COPs within a wafer side than 100 was a defect-free layer, and the rate of an excellent article evaluated the evaluation by oxide-film pressure-proofing here noting that even 90% or more of depth was a defect-free layer.

[0058]

[Table 1]

窒素濃度 (atoms/cm^3)	冷却速度 (℃/min)	酸素濃度 (ppma)	無欠陥層深さ (μm)		内部微小欠陥密度 (ケ/cm^3)
			COP数による評価	酸化膜耐圧特性による評価	
3×10^{14}	2.3	10	12	12	1×10^{9}
		14	6	6	8×10^{9}
		16	2	3	9×10^{9}
	3.5	10	12	12	2×10^{9}
		14	12	7	9×10^{9}
		16	12	5	1×10^{10}
3×10^{13}	2.3	14	2	3	1×10^{9}
	3.5	12	9	6	3×10^{9}
		16	6	3	9×10^{9}
2×10^{12}	3.5	12	7	3	7×10^{8}
無し	2.3	14	0.3	0.5	2×10^{8}
	3.5	10	0.1	0.5	5×10^{7}

[0059] Compared with the wafer by which only the oxygen density and cooling rate of the former [wafer / which was produced from the single crystal which the nitrogen concentration concerning this invention was controlled and was raised from Table 1] were controlled, it turns out that the defect-free layer depth and internal minute defect density are improving remarkably. Moreover, it plotted to drawing 1 by making into the defect-free layer depth what shows the low value among evaluation according the defect-free layer depth to the number of COPs, and evaluation by oxide-film pressure-proofing. Drawing 1 shows that the controllable range of the defect-free layer depth and internal minute defect density has expanded the wafer concerning this invention of an example far compared with the conventional wafer of the example of comparison.

[0060] In addition, this invention is not limited to the above-mentioned operation gestalt. The above-mentioned operation gestalt is instantiation, and no matter it may be what thing which has the same composition substantially with the technical thought indicated by the claim of this invention, and does the same operation effect so, it is included by the technical range of this invention.

[0061] For example, it faces raising the silicon-single-crystal rod which doped nitrogen with the Czochrlski method in this invention, it is not asked whether the magnetic field is impressed to the melt, and the MCZ method for impressing the so-called magnetic field is also included in the Czochrlski method of this invention.

[0062] Moreover, also in gettering heat treatment or device manufacture heat treatment

performed to the silicon-single-crystal wafer, the above-mentioned operation gestalt is instantiation to the last, and can be suitably changed with the specification of the device manufactured etc.

[0063]

[Effect of the Invention] By raising the silicon-single-crystal rod which doped nitrogen, and controlling the nitrogen concentration in a Czochralski crystal, an oxygen density, and the cooling rate in a crystal growth by the Czochrlski method, the defect-free layer depth after gettering heat treatment can be made into the range of 2-12 micrometers, and 1x108 to 2x1010 internal minute defect density /after gettering heat treatment or device manufacture heat treatment can be controlled by this invention in 3 and the latus range cm. Therefore, the silicon-single-crystal wafer of this invention has a large device production field, it becomes a thing with high gettering capacity, and the utility value on industry is very high.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing having shown the defect-free layer depth and internal minute defect density of a silicon-single-crystal wafer in various parameter value.

[Drawing 2] It is drawing having shown typically the crystal defect in a silicon-single-crystal wafer, and the appearance of a precipitation-of-oxygen object, and (a) is drawing having shown the situation in the wafer concerning this invention, and (b) is drawing having shown the situation in the wafer of the wafer by the conventional process.

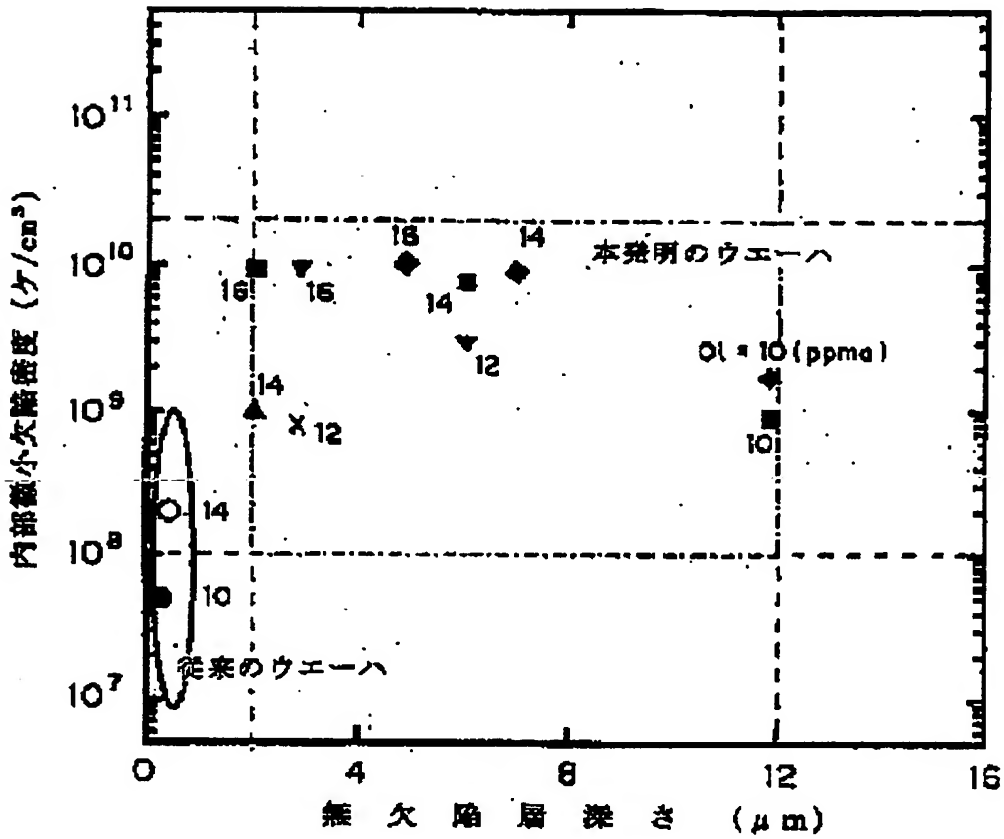
[Drawing 3] It is drawing having shown the relation between the nitrogen concentration

of a silicon-single-crystal wafer, and the width of face of the OSF field on the front face of a wafer.

[Drawing 4] It is drawing having shown the relation of the nitrogen concentration of a wafer and SF density on the front face of a wafer at the time of growing epitaxially on the front face of a silicon-single-crystal wafer.

DRAWINGS

[Drawing 1]



■ 窒素濃度3×10^{14}atoms/cm^{3}，冷却速度2．3℃/min

◆ 窒素濃度3×10^{14}atoms/cm^{3}，冷却速度8．5℃/min

▲ 窒素濃度3×10^{13}atoms/cm^{3}，冷却速度2．3℃/min

▼ 窒素濃度3×10^{13}atoms/cm^{3}，冷却速度8．5℃/min

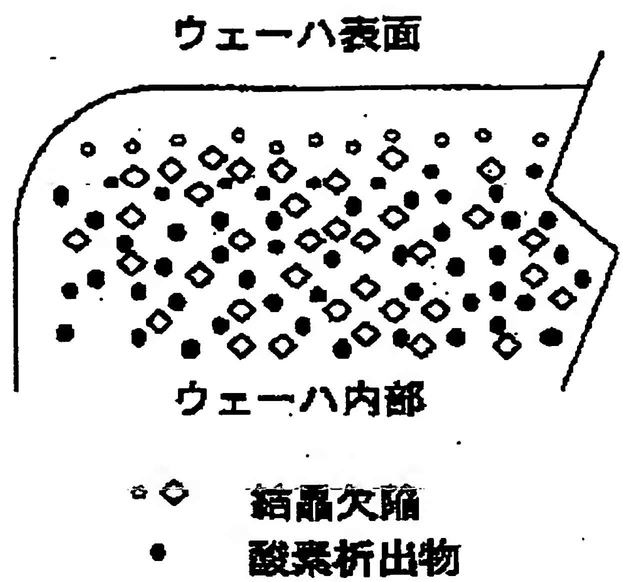
× 窒素濃度2×10^{12}atoms/cm^{3}，冷却速度8．5℃/min

○ 窒素ドープなし，冷却速度2．3℃/min

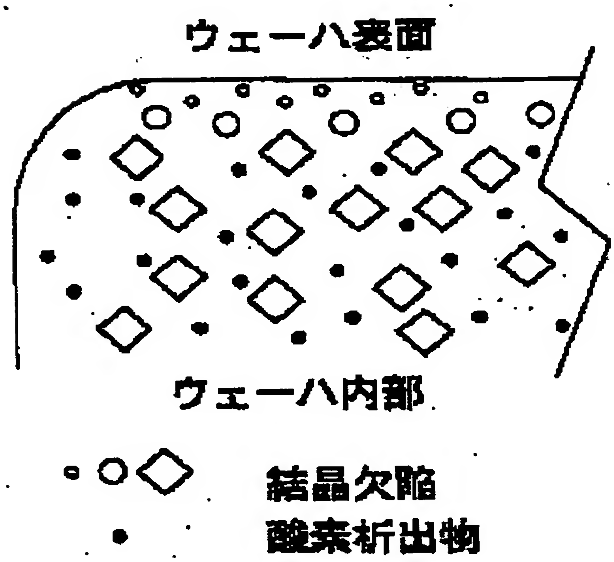
● 窒素ドープなし，冷却速度8．5℃/min

[Drawing 2]

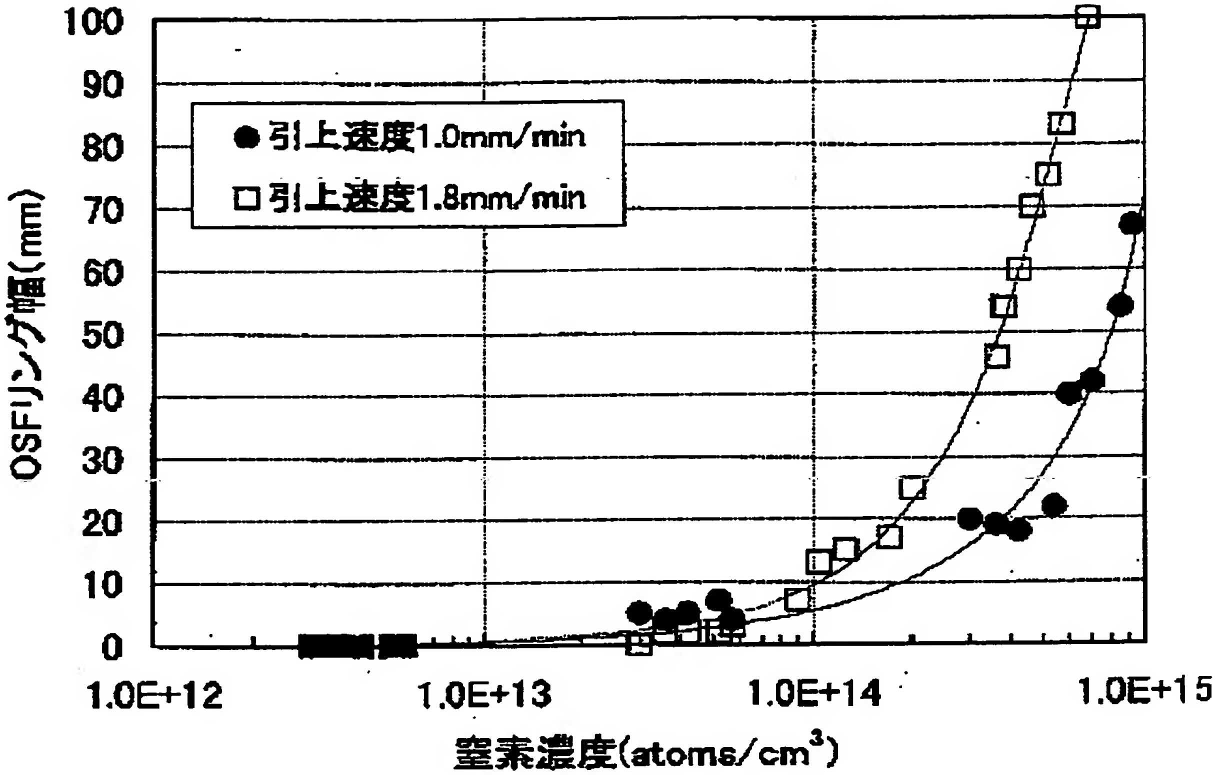
(a)



(b)

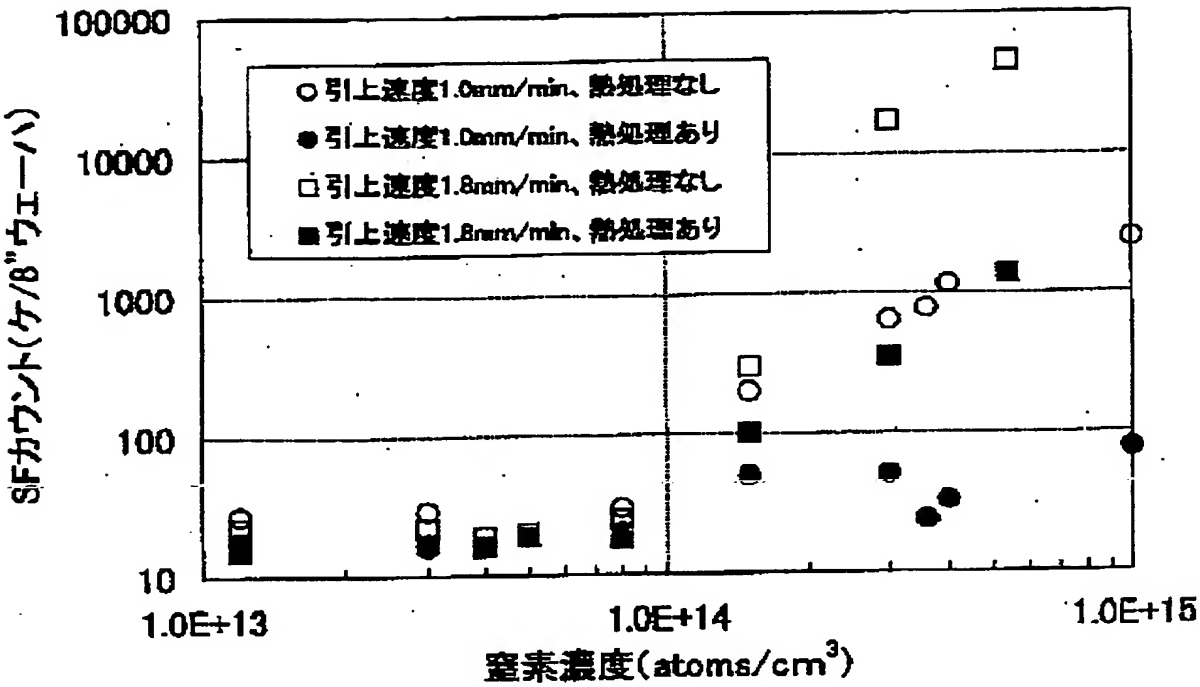


[Drawing 3]



100
90
80
70
60
50
40
30
20
10
0
OSFリング幅(mm)
●引上速度1.0mm/min
□引上速度1.8mm/min
1.0E+12
1.0E+13
1.0E+14
1.0E+15
窒素濃度(atoms/cm3)

[Drawing 4]



[Translation done.]